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A THEORETICAL SEARCH FOR SUPER-VELOCITY SEMICONDUCTORS.(U)
JAN 78 M A LITTLEJOHN, J R HAUSER N00014-76-C-0480

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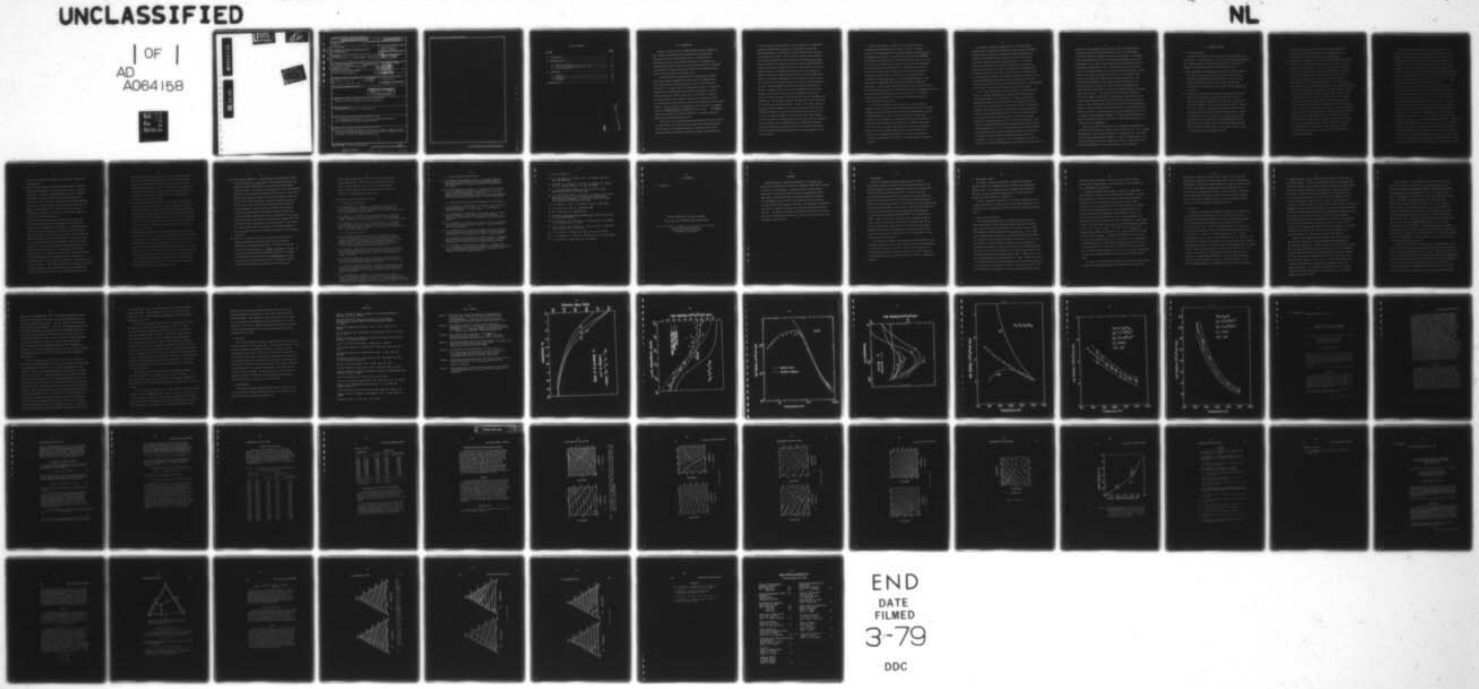

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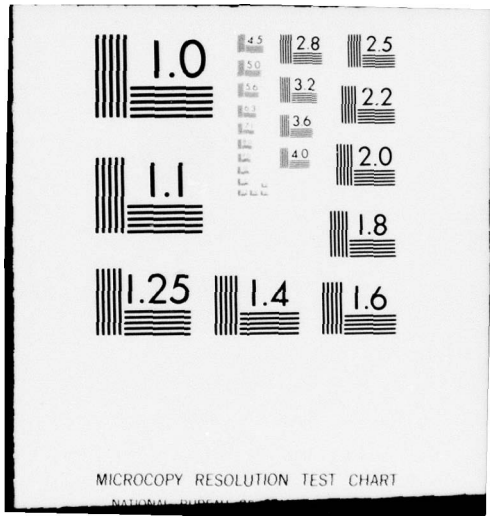
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This report presents the results of research on carrier transport in III-V semiconducting compounds and alloys and the performance of microwave devices fabricated from those compounds and alloys.

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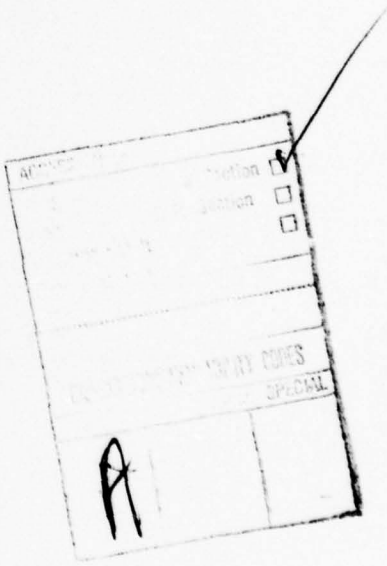

1.0 INTRODUCTION

During the past four years an ONR-sponsored research program has been underway at North Carolina State University which basically involves the use of the Monte Carlo method to study high-field transport properties of semiconductor materials. The emphasis has been directed toward the study of ternary and quaternary III-V compounds in an attempt to identify specific materials with desirable electronic properties for microwave device applications.

A substantial effort has been devoted to developing a complete Monte Carlo computer program which can be used as a predictive tool in the study of hot electron transport, as well as low field ohmic transport, in a general class of semiconductor materials. We presently believe that the capabilities which have been developed so far under ONR sponsorship are second to none within the scientific community, and that the bulk static transport properties of two general classes of quaternary III-V semiconductors can be predicted using our computational methods. These two classes of quaternary materials consist of compounds of the form $A^{III}_{1-x}B^{III}_{x}C^{V}_{1-y}D^{V}_{y}$ and $A^{III}_{x}B^{III}_{y}C^{III}_{z}D^{V}$ (or conversely $A^{III}B^{V}_{x}C^{V}_{y}D^{V}_{z}$), which can be specified to include any binary or ternary compound as a subset of these general material forms.

The accuracy of the computational program depends on several factors. One major factor is the way in which the quaternary material parameters are calculated. The technique depends on a knowledge of the binary material parameters and either theoretical models or experimental data

for the ternary material parameters. This information is coupled into a general interpolation procedure for calculating the quaternary material parameters, from which the transport properties are obtained in the Monte Carlo method. This work has culminated in the prediction that specific compositions of the quaternary compound $Ga_{1-x}In_xP_{1-y}As_y$ lattice-matched to InP substrates possess transport properties having distinct advantages over GaAs [1] for device applications. In the past eighteen months considerable experimental work on this compound has shown the material to indeed be promising for many device applications. However, the complete advantages due to the predicted superior transport properties have not been realized at the present time, and efforts to make a microwave MESFET have only been partially successful [2]. However, it appears that many of the device problems can be overcome through the refinement of the materials technology, and there are reasons to remain optimistic that the predicted material advantages will be borne out. In the authors' opinion the influence of alloy scattering still remains an unanswered question. However, very recent results on $Al_{1-x}Ga_xAs$ strongly suggest that our approach which uses the electron affinity difference for the alloy scattering potential is correct [3]. It is to be noted that these recent results have come about through careful refinement of the growth process to the point where pure material can be achieved. Then, by examining the low temperature (77K) Hall mobility, the effects of alloy scattering can be separated from those due to ionized impurity scattering, and are in good agreement with our previous models.

During the past year, one phase of our research has been to investigate other quaternary III-V systems. In fact, a complete survey of the fifteen major quaternary systems of the form $A_{1-x}B_xC_{1-y}D_y$ and $A_xB_yC_zD$ has been made. The systems are composed of the compounds from the group III atoms Al, Ga, and In and the group V atoms P, As, and Sb. Some of these systems, to be discussed later, also have desirable material properties for electron devices. However, we have taken a wait-and-see approach before submitting this data for publication in the open literature, since we feel that it is imperative for the calculations on $Ga_{1-x}In_xP_{1-y}As_y$ to be verified experimentally to some extent before suggesting other new quaternary material systems for development. Very recently, experimental work on the low field mobility of the ternary $Ga_{1-x}In_xAs$ lattice matched to InP has been reported as verification of our previous calculations for this material [4]. It should be remarked that much progress in the materials growth technology has led to these impressive results.

It has become apparent during the last year that a significant emerging research area is that of submicron device physics and technology. During the past grant period our research has been substantially shifted to emphasize this area and to begin a major effort in this field. We would like to concentrate on the physical processes which effect the operation of small devices and to begin to use the Monte Carlo method for this purpose. We plan to question based on first principles the physics of electron transport upon which the Monte Carlo method is based, and to investigate the fundamental limits of the validity of the Monte Carlo method as a technique for studying transport phenomena in general.

For example, one should probably begin by examining a basic premise of most traditional treatments of transport theory, including the Monte Carlo method, which separates the transport process into separate and non-interacting processes of drift in the field and scattering through a lattice or defect interaction. It has been pointed out that under the conditions of high electric fields and strong scattering rates that such an assumption is questionable [5], and these conditions could be met in small devices. Our plans extend to investigations of other areas including statistical concepts, such as fluctuation phenomena, modifications of collision interactions and interaction time field effects, velocity overshoot effects, two-dimensional device effects, and the general examination of device concepts.

There is one final point to be discussed here. The Monte Carlo method is generally considered as a single-particle description of transport phenomena. For this reason, it has been stated that the Monte Carlo method will have difficulties in treating small device effects because electron-electron interactions cannot be conveniently included, and these will become important due to scaling rules which generally require higher doping levels as device dimensions decrease. Now, besides the Monte Carlo method, there are two other methods proposed for application to and study of small device problems. These methods are the drifted-Maxwellian approximation [6] and the iterative integral approach [7]. Both of these techniques also have limitations at high doping primarily because degenerate statistics are difficult to include and are of necessity fundamentally neglected in the formulations. Also, it seems to us to be premature at this time to argue in favor of the drifted-Maxwellian approximation over the other two

methods as being the high electron density limit to the distribution function [8], and at the same time argue in favor of a reevaluation of physical concepts as applied to small electron devices. For example, the drifted-Maxwellian may be a valid velocity distribution function at high doping, but it is not a valid momentum distribution function due to non-parabolic band effects. Also, the question of the use of the concept of a distribution function must be raised when one beings to consider small devices where non-steady-state processes, such as velocity overshoot and time-dependent diffusion processes, become important. The Monte Carlo method does not necessarily involve the concept of the distribution function except in a self-consistent methodology, and should rightly be considered as the major fundamental approach to modeling small device physics. Our approach has been to begin to apply the Monte Carlo method to small devices by making major modifications to the computational techniques which are oriented toward treating such small devices. These modifications include the treatment of position-dependent electric field distributions and velocity-overshoot and diffusion-overshoot effects in general. The next step, which has been accomplished this year, is to also include degenerate statistics in the scattering processes. We believe we have made a major contribution in this regard, and papers are being prepared for publication.

Thus, a major goal of this research is to examine the application of the Monte Carlo method to the study of small electron devices. It is strongly believed that of the possible techniques to be appropriate for such studies that the Monte Carlo method will again, as it has in the past, prove to be the more complete and accurate computational method to study transport and hot electron phenomena in the next generation of electron devices.

2.0 RESEARCH RESULTS

2.1 Review of Progress

This section contains a brief discussion of work performed during the past year. Also included are a list of publications and presentations, and a summary of papers in progress for publication. Finally, the appendices include manuscripts published during this year.

1) The calculation of iso-bandgap and iso-lattice constant contours for III_2-V_2, III_3-V_1, and III_1-V_3 quaternary alloys has been completed and published during 1978 [9,10]. We have received several requests for reprints, and a request from Rockwell International for additional calculations in the $Al_{1-x}Ga_xAs_{1-y}Sb_y$ quaternary.

2) A systematic examination of the transport properties of fifteen quaternary alloys (nine III_2-V_2 alloys and three each of the III_3-V_1 and III_1-V_3 alloys) has been carried out. The group III elements considered are Al, Ga, and In while the group V elements are P, As, and Sb. Some systems have properties which look very promising, especially for transferred electron devices. None of the materials seem to be superior to $Ga_{1-x}In_xP_{1-y}As_y$ for FET's, but there are several systems possessing high peak velocities, high saturated velocities, and low threshold fields which makes these attractive for TED devices. For example, specific systems are $Ga_{1-x}In_xP_{1-y}Sb_y$, $Ga_{1-x}In_xAs_{1-y}Sb_y$ and

We plan to submit this work for publication, but would like to wait for more advanced materials growth technology and the measurement of material parameters for $Ga_{1-x}In_xP_{1-y}As_y$.

3) The Monte Carlo program has been modified to account for the effects of degeneracy in heavily-doped materials. At low electric fields, when the electron temperature and lattice temperature are equal, the principle modification is the incorporation in the scattering rates of an occupancy factor 1-f(E'), where E' is the electron energy after scattering and f(E') is the Fermi-Dirac energy distribution function with parameters E_f and T_e. At low fields, these parameters can be determined from the free carrier concentration n and the average carrier energy $\frac{3}{2} kT_e$. At high electric fields the hot electron distribution function, and thus the occupancy factor, is unknown, but the Fermi-Dirac distribution function is assumed to be a reasonable first approximation. However, in this case the Fermi energy and the electron temperature cannot be determined a priori, since the electron energy is unknown. The approach which we have taken is to perform the Monte Carlo calculation iteratively, calculating the average energy in each iteration and using this calculated value along with the electron concentration to up-date E_f, T_e, and the occupancy factor 1-f(E'). The iterative process is continued until self-consistent values of E_f, T_e, and the average energy are obtained. These values are then used in the transport calculations.

Several other modifications have also been completed in connection with the simulation of heavily-doped materials. For example, the inclusion of a transverse magnetic field allows the calculation of Hall mobility, and the required modification of Einstein's relation to account for degeneracy allows the accurate estimation of drift velocity at low applied fields. Some of the results of this work have been presented at the Hot Electron Workshop at Cornell University, Aug. 17-18, 1978 and at the 7th International Symposium on GaAs and Related Materials in St. Louis, Sept. 24-27, 1978. Two journal articles are now in preparation.

4) The Monte Carlo method has been applied to the determination of the spatial distribution function and its temporal evolution for hot electrons. Among other things, transients in carrier velocity and the diffusion process itself can be investigated in terms of the instantaneous mean m(t) and variance s(t) of this distribution. Velocity overshoot phenomena such as obtained by other techniques [11] have been observed and can be studied at a more basic level by this approach. We have also observed both an overshoot and an undershoot in the diffusion rate or diffusion coefficient D (here regarded as a function of time through the definition $D(t) = \frac{1}{2}\frac{d}{dt}s^2(t)$). Transients in both diffusion coefficient as well as carrier velocity persist over distances traversed by carriers which are comparable to important dimensions in sub-micron devices, and may have important implications in the theory and design of such devices. Thus, these transient phenomena warrant further study. Preliminary results from this work were presented at the 1978 Hot Electron Workshop at Cornell,

and a more complete discussion will be contained in a paper now in preparation.

5) The Monte Carlo program is currently being modified to allow the addition of a sinusoidal time-varying electric field. The basic approach is to construct a pseudo-ensemble of carrier histories by stacking one-period segments from a single long-duration simulation. This modification will allow Monte Carlo determination of the basic frequency response characteristics of materials, and should provide information as to their performance at mm- and sub-mm wave frequencies. This work is in the initial stages and no results have yet been obtained.

6) Several other areas are being investigated which involve major modifications in the Monte Carlo technique. For example, the incorporation of boundaries in one-dimension is being investigated in order to allow simulation of materials with finite thickness. This could become very important in the study of sub-micron devices. Other modifications, which will be discussed in the next section, are the incorporation of position-dependent scattering rates and the further investigation of the position-dependent electric field problem. Also, new models for ionized-impurity scattering and electron-electron scattering which examine basic statistical factors in the fundamentals of these problems are under investigation.

7) Preliminary work on the transport properties of II-IV-V_2 chalcopyrites has been completed. Bulk transport properties of $ZnSiAs_2$, a material which is being grown in our laboratories, have been studied and certainly look very interesting. The static velocity-field curve

resembles that of InP in many respects. However, there are major uncertainties in the band structure of this particular compound and of the chalcopyrites in general. We feel that we should be careful in presenting such results since they are only speculative at present. Also, there are major materials growth problems in the chalcopyrites which must be solved before these compounds will become useful electronic materials.

8) Work on traditional velocity-overshoot calculations (11) has been completed for $Ga_{1-x}In_xP_{1-y}As_y$. The results suggest that if high-mobility material with a band-gap of about 1 eV could be grown on InP substrates, then velocity overshoot effects should be observable in devices with channel lengths between 0.5 μm - 1.0 μm. The extent of the overshoot is substantially greater than that for GaAs or InP in this quaternary. Other quaternaries and ternaries are being examined at this time.

9) A two-dimensional device model has been developed and is now being further refined. The computational procedure is very similar to that being used by H. L. Grubin at United Technologies Research Center. The modifications now being incorporated involve the use of the quasi-linearization technique which has been utilized at N. C. State University to model solar cells [12]. We believe this technique will enhance the capabilities of the device program. The long-term goal is to provide a device program which will interact with the Monte Carlo program to provide a self-consistent solution for transport and terminal properties of sub-micron devices.

10) Work has been carried out to experimentally and theoretically study alloy scattering in $Ga_{1-x}In_xP_{1-y}As_y$. The experimental work has been supported by AFOSR and was done in conjunction with the Research Triangle Institute. The results were presented at the 7th International Symposium on GaAs and Related Compounds held in St. Louis, Sept. 24-27, 1978, and they appear to suggest that alloy scattering, or some other form of defect scattering having a temperature dependence similar to alloy scattering, is greatly affecting the low-field mobility in this quaternary. One such mechanism could be space-charge or precipitate scattering [13]. This point is made in light of the results presented by Pearsall [4] at the same meeting on $Ga_{.47}In_{.53}As$ (lattice matched to InP) which were interpreted to suggest that alloy scattering was *not significant* (at room temperature) in this ternary. It is very probable that future advances in growth technology for $Ga_{1-x}In_xP_{1-y}As_y$ will lead to substantial improvements in the transport properties.

11) The work on negative resistance in the central $\Gamma(000)$ valley of compound semiconductors has been completed and accepted for publication in Solid-State Electronics. The effect is real and our previous interpretation of it stands as originally reported. The inclusion of the p-state mixing phenomena resulted in no changes in the original conclusions, and the phenomenon appears to have other previously unforseen implications. For example, velocity overshoot in materials whose peak velocity is determined by

central valley scattering is different from that of materials such as GaAs and InP. The overshoot seems to persist for much longer times in such materials. Thus, it is possible that central valley-dominated compound semiconductors could be very important in sub-micron device applications.

2.2 Publications and Presentations in 1978

A. Publications During 1978.

1) M. A. Littlejohn, J. R. Hauser, T. H. Glisson, D. K. Ferry, and J. W. Harrison, "Alloy Scattering and HIgh Field Transport in Ternary and Quaternary III-V Semiconductors", Solid-State Electronics, vol. 21, pp. 107-114, January, 1978.

2) T. H. Glisson, J. R. Hauser, M. A. Littlejohn, and C. K. williams, "Energy Bandgap and Lattice Constant Contours of III-V Quaternary Alloys", Journal of Electronic Materials, vol. 7, pp 1-16, January, 1978.

3) C. K. Williams, T. H. Glisson, J. R. Hauser, and M. A. Littlejohn, "Energy Bandgap and Lattice Constant Controus of III-V Quaternary Alloys of the Form $A_xB_yC_zD$ or $AB_xC_yD_z$", Journal of Electronic Materials, vol. 7, pp 639-646, July, 1978.

B. Presentations During 1978.

1) M. A. Littlejohn, "Monte Carlo Approaches to Hot Electron Effects - A Review of the Application of the Monte Carlo Method to Carrier Transport Studies in Semiconductors", Invited Paper presented at the Workshop on Hot Electron Phenomena in Semiconductors held at Cornell University, August 17-18, 1978, sponsored jointly by the Office of Naval Research and the Army Research Office.

2) C. K. Williams, "Comparison of Techniques for Estimation of Diffusion Coefficient From Monte Carlo Data", presented at the Workshop on Hot Electron Phenomena in Semiconductors held at Cornell University, August 17-18, 1978.

3) T. H. Glisson, "Spatial Distribution Functions for Hot Electrons", presented at the Workshop on Hot Electron Phenomena in Semiconductors held at Cornell University, August 17-18, 1978.

4) J. R. Hauser, "Degenerate Statistics and Ionized Impurity Scattering in Monte Carlo Calculations for GaAs", presented at the Workshop on Hot Electron Phenomena in Semiconductors held at Cornell University, August 17-18, 1978.

5) M. A. Littlejohn, R. A. Sadler, T. H. Glisson, and J. R. Hauser, "Carrier Compensation and Alloy Scattering in $Ga_{1-x}In_xP_{1-y}As_y$ Grown by Liquid Phase Epitaxy", paper presented at the 7th International Symposium on GaAs and Related Compounds held in St. Louis, Mo., September 24-27, 1978.

C. Papers Accepted for Publication.

1) J. R. Hauser, T. H. Glisson, and M. A. Littlejohn, "Negative Resistance and Peak Velocity in the Central (000) Valley of III-V Semiconductors, accepted for publication in Solid-State Electronics.

2) M. A. Littlejohn, R. A. Sadler, T. H. Glisson, and J. R. Hauser, "Carrier Compensation and Alloy Scattering in $Ga_{1-x}In_xP_{1-y}As_y$ Grown by Liquid Phase Epitaxy", accepted for publication in the Proceedings of the 7th International Symposium on GaAs and Related Compounds-Institute of Physics publication.

D. Papers in Preparation and To Be Submitted for Publication.

1) L. A. Arledge, M. A. Littlejohn, T. H. Glisson, and J. R. Hauser, "Velocity Overshoot in $Ga_{1-x}In_xP_{1-y}As_y$", to be submitted to Electronics Letters.

2) L. A. Arledge, M. A. Littlejohn, T. H. Glisson, and J. R. Hauser, "Velocity Overshoot in III-V Semiconductors Dominated by Scattering in the Γ-Valley", to be submitted to Applied Physics Letters.

3) T. H. Glisson, C. K. Williams, J. R. Hauser, and M. A. Littlejohn, "Monte Carlo Calculation of Hall Mobility", to be submitted to Solid-State Electronics.

4) C. K. Williams, T. H. Glisson, J. R. Hauser, and M. A. Littlejohn, "Monte Carlo Simulation of Low Field Transport in Heavily Doped Semiconductors", to be submitted to Journal of Applied Physics.

5) C. K. Williams, T. H. Glisson, J. R. Hauser, and M. A. Littlejohn, "Monte Carlo Investigation of Hot-Electron Transport in Heavily-Doped Materials", to be submitted to Applied Physics Letters.

6) T. H. Glisson, C. K. Williams, R. A. Sadler, J. R. Hauser, and M. A. Littlejohn, "Time-Dependent Diffusion in Compound Semiconductors and Its Relationship For Sub-Micron Device Performance", to be submitted to Journal of Applied Physics.

2.3 List of References

1) M. A. Littlejohn, J. R. Hauser, and T. H. Glisson, Appl. Phys. Lett. 28 458 (1977).

2) H. Morhoc, J. T. Andrews, Y. M. Houng, R. Sankaran, S. G. Bandy, and G. A. Antypas, Electron. Lett. 14 448 (1978).

3) L. F. Eastmann and A. Chandra, Cornell University, private communication submitted for publication.

4) T. P. Pearsall, R. Bisaro, P. Merenda, G. Laurencin, and R. Ansel, paper II6. presented at the 7th International Symposium on GaAs and Related Compounds, St. Louis, Mo., Sept. 24-27, 1978, to be published in conference proceedings.

5) J. R. Barker, J. Phys. C: Solid-State Physics 6 2663 (1973).

6) R. Stratton, Proc. Roy. Soc. A246 406 (1958).

7) H. F. Budd, Phys. Rev. 158 798 (1967).

8) W. Fawcett, Electrons in Crystalline Solids, International Centre for Theoretical Physics.

9) T. H. Glisson, J. R. Hauser, M. A. Littlejohn, and C. K. Williams, Jour. Electron. Mat. 7 1 (1978).

10) C. K. Williams, T. H. Glisson, J. R. Hauser, and M. A. Littlejohn, Jour. Electron. Mat. 7 639 (1978).

11) J. Frey and T. J. Maloney, Jour. Appl. Phys. 48 781 (1977).

12) E. D. Graham and J. R. Hauser, Solid-State Electron. 15 303 (1972).

13) L. R. Weisberg, J. Appl. Phys. 33 1817 (1962).

3.0 APPENDICES

3.1 Appendix A

CARRIER COMPENSATION AND ALLOY SCATTERING IN $Ga_{1-x}In_xP_{1-y}As_y$ GROWN BY LIQUID PHASE EPITAXY

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ABSTRACT

Carrier mobilities achieved experimentally in $Ga_{1-x}In_xP_{1-y}As_y$ alloys are considerably less than those predicted by Monte Carlo transport calculations. In this paper, a comparison between the temperature dependence of electron Hall mobility measured experimentally on LPE-grown samples and calculated from a Monte Carlo method is presented. The experimental data is obtained from samples which are *n-type* and are grown on semi-insulating InP substrates. The theoretical calculations are based on a diffusion coefficient estimator for calculation of Hall mobility. An analysis of the data indicates that both alloy scattering and carrier compensation are necessary to explain the observed temperature dependence of Hall mobility.

1. Introduction

The III-V quaternary alloy $Ga_{1-x}In_xP_{1-y}As_y$ has received considerable attention recently due to many desirable electronic and material properties, and this compound has been used in a wide variety of device-related studies (Clawson 1978). In spite of the wide variety of developed applications, the desirable transport properties proposed for this material based on calculations using the Monte Carlo method (Littlejohn et al. 1977a) have not been fully realized (Morkoc et al. 1978, Houston et al. 1978). In particular, the reported Hall mobilities have been considerably lower than predicted, and room temperature electron concentrations below about $1x10^{16} cm^{-3}$ have been difficult to achieve. Much of the work has been done using liquid-phase epitaxy (LPE). However, the electron concentrations are much larger for the quaternary than those usually achieved for LPE growth of the binary compounds GaAs and InP, even though the starting constituent source materials used to grow the quaternary are of the same purity as those used for growth of the binaries.

In this paper a comparison between experimental Hall mobilities of LPE-grown quaternary layers on InP substrates and those calculated from the Monte Carlo method is presented. Based on this comparison it is concluded that both carrier compensation as well as alloy scattering are contributing to the low-field Hall mobility and to its temperature dependence.

2. Experimental Aspects

The samples studied in this paper were grown by liquid phase epitaxy at 660°C in a standard horizontal slider system (Phatak and Harrison 1978). The as-grown layers were undoped, and the substrate material was semi-insulating Fe-doped InP in a (111)B orientation. Typical layer thicknesses were around 10 μm.

The Hall measurements were made in a variable temperature cryostat between 77K and 300K. A standard Van der Pauw sample geometry was used, and contacts to the samples were made with an In-Sn alloy (Houston et al. 1978).

3. Monte Carlo Calculations

The calculations presented in this paper were obtained by the Monte Carlo method, using a program described previously (Littlejohn et al. 1977a). Of particular importance is the method used to obtain the quaternary material parameters for $Ga_{1-x}In_xP_{1-y}As_y$. This is done by an interpolation procedure which is based on an assumed knowledge of the constituent binary material parameters of, in this case, GaAs, InAs, InP, and GaP. While much needs to be done to further validate this interpolation procedure, it has proved useful in calculating energy band gap and lattice constant (Glisson et al. 1978, Moon et al. 1974) as well as electron effective mass (Restorff et al. 1978). In these cases it has led to good agreement with experimental data. Figure 1 shows the results of a calculation for the Γ-valley electron effective mass in $Ga_{1-x}In_xP_{1-y}As_y$ as a function of As composition for layers lattice-matched to InP. The three different curves represent calculations based on different values

of binary material parameters. However, for $y \geq 0.5$ the effective mass does not strongly depend on the uncertainty in the InP effective mass (y=0)(Maloney and Frey 1977).

In general, the Monte Carlo method is difficult to apply with good statistical accuracy at low fields and low temperatures. However, this problem can be overcome to a large extent by using statistical estimators for the diffusion coefficients (Canali et al. 1975). In addition, the present program has been further modified to include the effects of heavy doping as well as to use crossed electric and magnetic fields for the computation of Hall mobility, since it is Hall mobility and not drift mobility that is usually measured. The program details will be presented in a future publication. Heavy doping effects can be important in $Ga_{1-x}In_xP_{1-y}As_y$ alloys having small effective masses such as shown in Figure 1. For GaAs, with $m^*=0.063\ m_o$, the conduction band effective density of states is about $4\times10^{17}cm^{-3}$ at 300K. From the values in Figure 1 a number of $1.65\times10^{17}cm^{-3}$ for the density of states of a quaternary with y=0.7 is calculated. As the temperature is decreased to 77K, the conduction band effective density of states is reduced to $5\times10^{16}cm^{-3}$ for GaAs and to $2.1\times10^{16}cm^{-3}$ for the quaternary. Thus one could expect degenerate statistics to be important in determining the quaternary transport properites for presently achievable doping levels.

The Monte Carlo method has the additional feature that very detailed transport and scattering factors can be included in the calculations.

These factors include such band structure effects as p-state mixing and band non-parabolicity (Fawcett et al. 1970). Also, the Monte Carlo method takes into account thermal stimulation at temperatures above 300K of carriers into higher-lying conduction band minima (Rode 1975). If care is taken in assuring statistically accurate estimates in the Monte Carlo method, then the technique should be accurate and very complete, and as convenient as techniques based on classical transport analysis and the use of other numerical methods (Rode 1975).

4. Discussion

The use of the Monte Carlo method for calculating Hall mobility was first examined by considering data for GaAs since it was felt that values for all important transport coefficients and material parameters were reasonably well known (Rode 1975, Littlejohn et al. 1977b, Kratzer and Frey 1978). Figure 2 shows Hall mobility as a function of free electron concentation for GaAs at 300K for a compensation ratio of 1 (i.e. $N^+ + N^-/n = 1$, where N^+ = ionized donor density, N^- = ionized acceptor density and n = free electron density). Shown for comparison in this figure is a range of experimental data, taken for convenience from the last two proceedings of this conference and the standard data from Sze, 1969. Care was taken to record only data reported as Hall mobility data. Also shown are the results of a calculation for Hall mobility based on an iterative integral method (Rode 1975). There are some discrepancies between these two approaches, as can be seen in this figure. For low carrier concentrations the discrepancies (about 13%) can be attributed

to slightly different values of bulk material parameters used in the two calculation methods. The material parameters used here in the Monte Carlo calculation have been chosen based on both low-field mobility values and on high field transport properties (Littlejohn et al. 1977b, Kratzer and Frey 1978). However, the Monte Carlo method will yield Hall mobilities at low carrier concentrations ($<10^{14}cm^{-3}$) well above 9000 cm^2/volt sec if slight adjustments in bulk parameters are made, and certainly the sensitivity of the Hall mobility in pure GaAs to slight variations in material parameters is well-recognized (Rode 1975). At high carrier concentrations ($>10^{16}cm^{-3}$) the deviations between these two computational methods are much more subtle. They are due to the way in which the ionized impurity scattering rate is corrected for degeneracy in the Monte Carlo method and this will be a subject for a future paper. However, in spite of the differences the authors believe that the Monte Carlo method is an accurate technique for calculating Hall mobility which gives agreement with experimental data over a wide range of carrier concentrations.

Figure 3 shows experimental Hall mobility data versus temperature for pure GaAs, along with the calculated temperature dependence of mobility based on both the iterative integral and the Monte Carlo method. Here the Monte Carlo method gives an excellent fit over the temperature range 150K-600K, while Rode has pointed out that the iterative integral lies about 10% above the experimental data in this range (Rode 1975). While we have not done so in this study, it should be pointed out that the Monte Carlo method can be extended to temperatures below 10K (Canali et al. 1975). Also, other GaAs material has been successfully studied by the Monte Carlo method, and the general use of the method appears to be well-justified.

Shown in Figure 2 is a calculation of the Hall mobility versus electron concentration at 300K for $Ga_{.27}In_{.73}P_{.4}As_{.6}$ based on the Monte Carlo method and the material parameter interpolation procedure described previously (Littlejohn et al. 1977a). Presently, to the authors' knowledge, the largest value of room temperature Hall mobility for any quaternary is about 6000 cm^2/volt sec with an electron concentration of about $7x10^{15}cm^{-3}$ (Houston et al. 1978). Figure 4 shows a summary of typical Hall mobility versus temperature for the quaternary (and the InP lattice-matched ternary $Ga_{.47}In_{.53}As$) taken in our laboratory and reported in the literature (Houston et al. 1975, Takeda et al. 1976). In general, the room temperature Hall mobilities seem to lie in the range of 3000-4000 cm^2/volt sec with electron concentrations of $(2\text{-}4)x10^{16}cm^{-3}$. Interestingly enough, the highest mobilities and lowest electron concentrations consistently seem to occur near the ternary boundaries for the quaternary, i.e. for either relatively low As or P compositions. This is suggestive of the influence of alloy scattering (Littlejohn et al. 1978).

To investigate the general problem of carrier compensation and alloy scattering in the quaternary $Ga_{1-x}In_xP_{1-y}As_y$ the Monte Carlo method was used to study several typical samples. Figure 5 illustrates the situation when an attempt was made to fit the data using either carrier compensation with no alloy scattering or alloy scattering with no carrier compensation. First, the alloy scattering potential (Littlejohn et al. 1978) was varied while keeping the compensation ratio equal to 1 (i.e. $N^+=N^-=n$) until agreement was obtained between the measured and calculated Hall

mobility at room temperature. Then the temperature dependence of Hall mobility was calculated, resulting in curve a) of Figure 5 which is in very poor agreement with the data. Curve b) results by removing alloy scattering from the calculation. First, the ionized impurity density was varied until agreement was achieved with the measured Hall mobility at room temperature, while keeping the free carrier density equal to its measured room temperature value. Curve b) is the resulting temperature variation of Hall mobility with only carrier compensation present. Again the agreement with experimental values at other temperatures is very poor, and it was concluded that neither alloy scattering nor carrier compensation could account for the measured temperature dependence of Hall mobility.

Next, an attempt was made to find a consistent set of values for both the alloy scattering potential and the ionized impurity density which would together give a good fit to the temperature dependence of Hall mobility. To do this two experimental points were chosen, one at 300K and one at about 150K. A detailed parameter study was made by varying the alloy scattering potential and ionized impurity density until a set of values for these two parameters which agreed with the measured values of both Hall mobility and electron concentration at the two temperature extremes. Then the complete Hall mobility versus temperature curve was calculated using these values. The results are shown in Figure 6. The Monte Carlo estimates lie within the dashed curves (several estimates were made at each temperature) while the bars indicate a 5% variation in the experimental data at the two temperature extremes. It should be pointed out that the fits are facilitated by the fact that the electron

concentration does not vary significantly for these quaternary samples between 100K-300K. The compensation ratio of 3.9 is very close to a sample with a very similar temperature dependence of mobility studied by Houston et al. 1978.

The calculations are more sensitive to the ionized impurity density than they are to the alloy scattering potential. Thus, it is not feasible to draw many conclusions from the actual value of the alloy scattering parameter shown in Figure 6. The value is larger than the proposed theoretical values for three different models (Littlejohn et al. 1978) by as much as 20% to 100%. There is another scattering mechanism which has the same temperature dependence of mobility as alloy scattering, which is often called space charge scattering (Weisberg 1962). If this mechanism were also present in these samples it would be difficult to detect from Hall measurements alone, but could effect the determination of alloy scattering potential by the technique used here. This added effect could be the result of precipitates, clustering, or other types of second-phase defects.

Other samples with similar Hall mobility temperature dependences have been studied with very similar results as given in Figure 6. In general for these quaternaries the weaker the temperature dependence of Hall mobility between about 100K-300K, the more important alloy scattering becomes.

It is interesting to consider those samples with a stronger temperature dependence in this temperature range. Figure 7 shows the results for a $Ga_{.47}In_{.53}As$ sample, which is a ternary in this quaternary system having a Hall mobility at room temperature larger than 8000 cm^2/volt sec (Morkoc 1978, Takeda 1978). For this case, the temperature dependence of Hall

mobility could be fit by the Monte Carlo method, but with an alloy scattering parameter essentially the same as that predicted by the theoretical model. The influence of alloy scattering in this ternary is less important in determining the Hall mobility than it is in the quaternary. This fact is somewhat surprising based on previous results for the scattering potentials in both ternary and quaternary alloys (Littlejohn et al. 1978).

5. Conclusions

Alloy scattering appears to play an important role in the low-field transport properties of $Ga_{1-x}In_xP_{1-y}As_y$. This conclusion is based on the data and calculations presented in this paper, as well as on other published Hall effect data. However, the accuracy of the calculations are predicated on the material parameter interpolation procedure, which is presently required for any transport calculations in this quaternary. Historically, the Monte Carlo method has become more useful in studying transport properties in compound semiconductors as accurate material parameters become available. The determination of the basic material parameters should be an important part of programs which attempt to obtain high-purity $Ga_{1-x}In_xP_{1-y}As_y$ quaternary alloys.

6. Acknowledgments

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References

Canali C, Jacoboni C, Nava F, Ottoviani G, and Alberigi-Quaranta A 1975 Phys. Rev. B 12 2265-84.

Clawson AR 1978 III-V Semiconductor Quaternary Alloy InGaAsP- A Bibliography (Technical Note 373 Naval Ocean Systems Center, San Diego).

Fawcett W, Boardman AD and Swain S 1970 J. Phys. Chem. Sol. 31 1963-90.

Glisson TH, Hauser JR, Littlejohn MA, and Williams CK 1978 J. Electron. Mat. 7 1-16.

Houston B, Restorff JB, Allgaier RS, Burke JR, Ferry DK, and Antypas GA 1978 Sol. St. Electron. 21 91-4.

Kratzer S and Frey Jeffrey 1978 J. Appl. Phys. 7 4064-70.

Littlejohn MA, Hauser JR, and Glisson TH 1977a Appl. Phys. Lett. 30 242-4.

Littlejohn MA, Hauser JR, and Glisson TH 1977b J. Appl. Phys. 48 4587-90.

Littlejohn MA, Hauser JR, Glisson TH, Ferry DK, and Harrison JW 1978 Sol. St. Electron. 21 107-14.

Maloney TJ and Frey Jeffrey 1977 J. Appl. Phys. 48 781-7.

Moon RL, Antypas GA, and James LW 1974 J. Electron. Mat. 3 635-43.

Morkoc H, Andrews JT, Houng YM, Sankaran R, Bandy SG, and Antypas GA 1978 Electron. Lett. 14 448-9.

Phatak SB and Harrison JW 1978 private communication

Restorff JB, Houston B, and Burke JR 1978 Appl. Phys. Lett. 32 189-90.

Rode DL 1975 Semiconductors and Semimetals: Vol. 10 (New York: Academic Press) p. 1.

Sze SM 1969 Physics of Semiconductor Devices (New York: Wiley) p. 40.

Takeda Y, Sasaki S, Imamura Y., and Takagi T 1976 J. Appl. Phys. 47 5405-8.

Weisberg LR, 1962 J. Appl. Phys. 33 1817-28.

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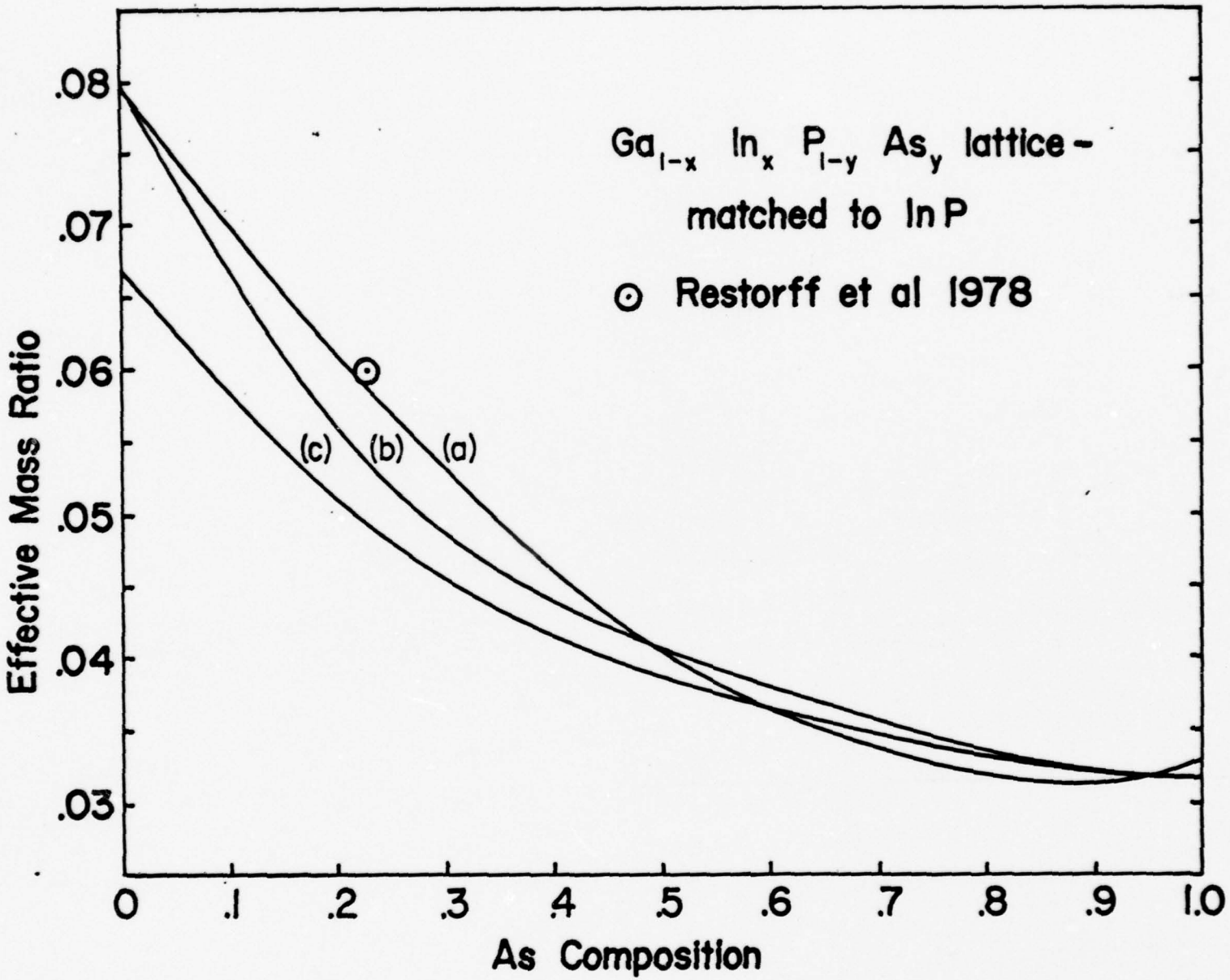
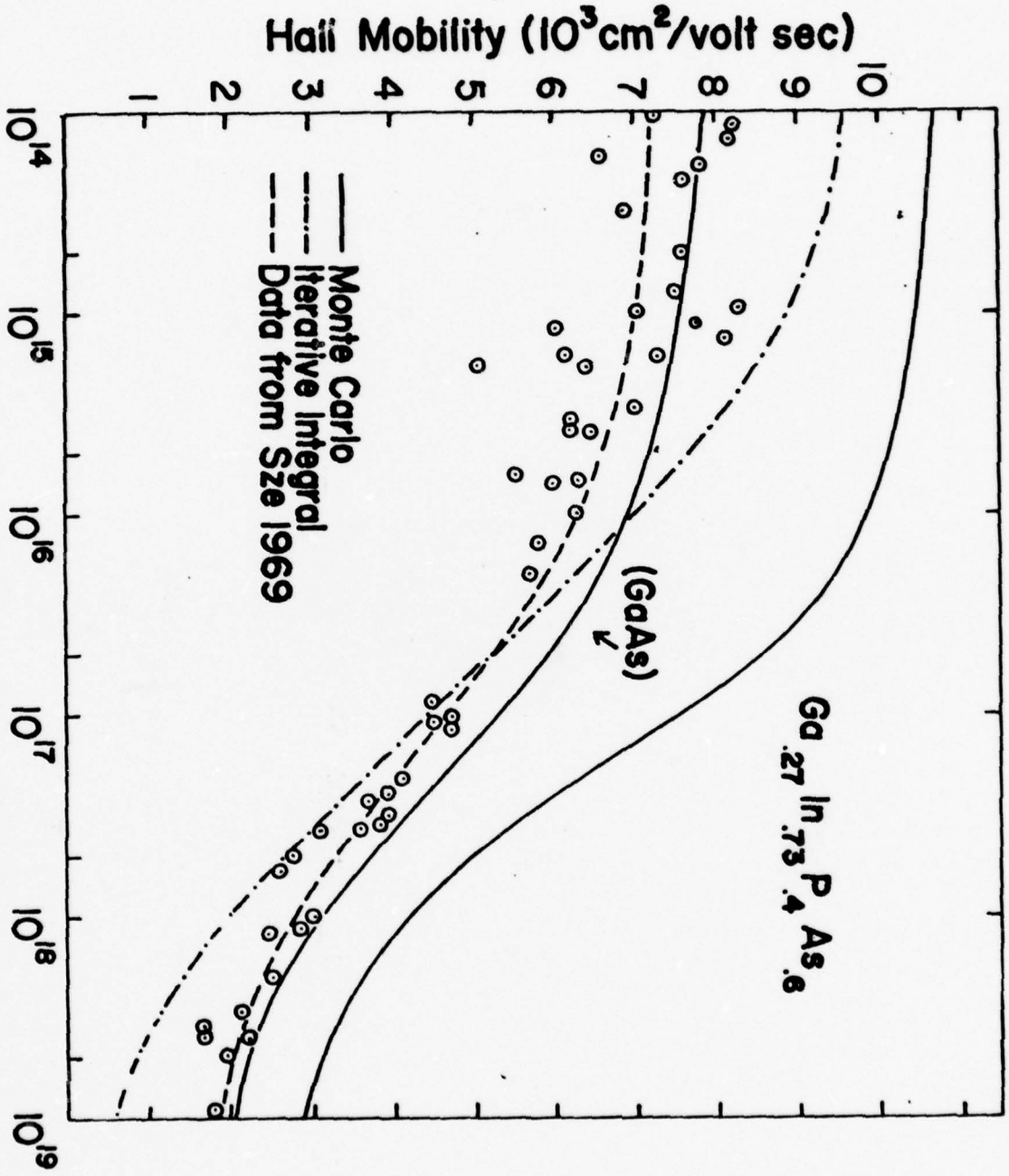
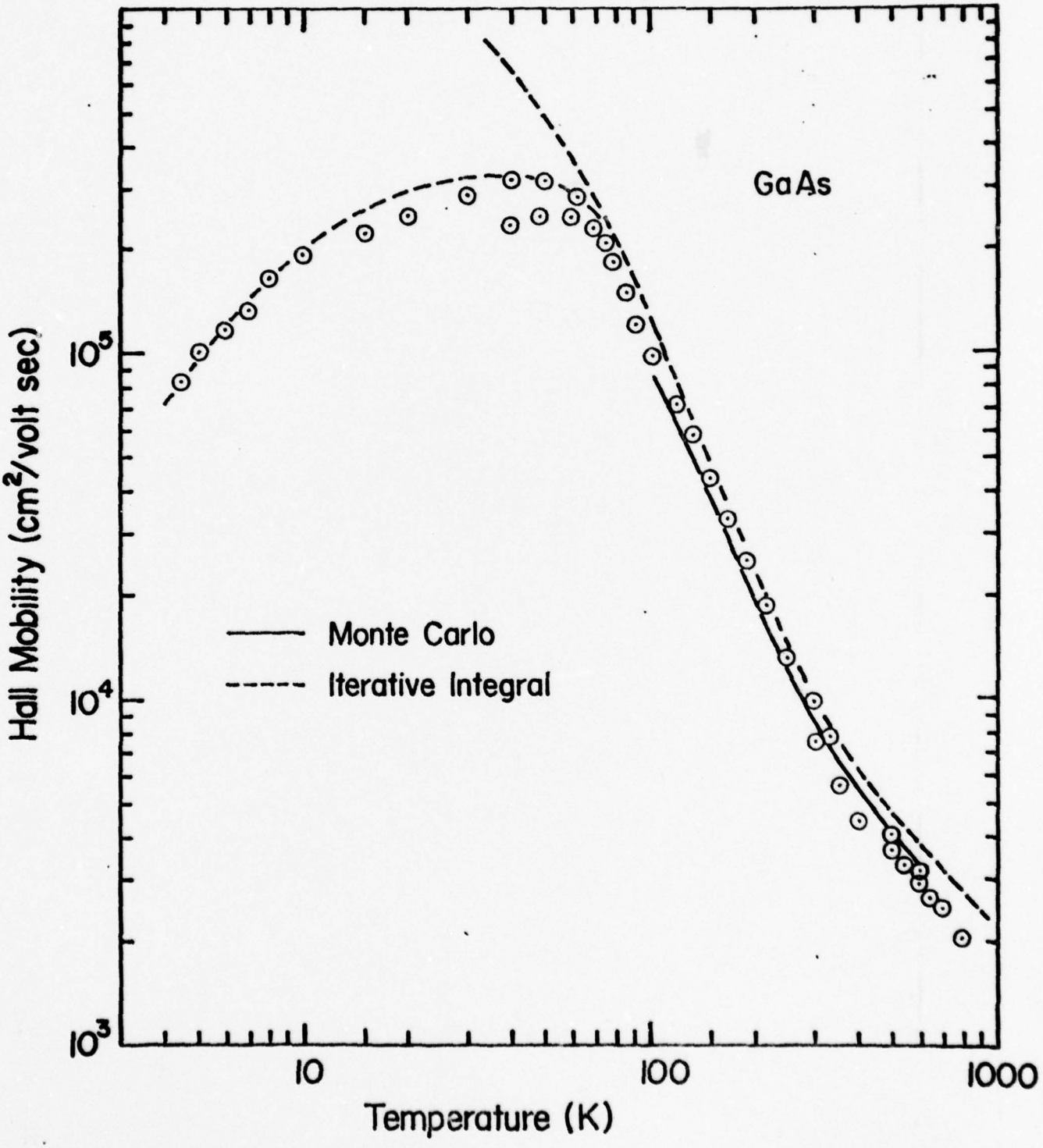
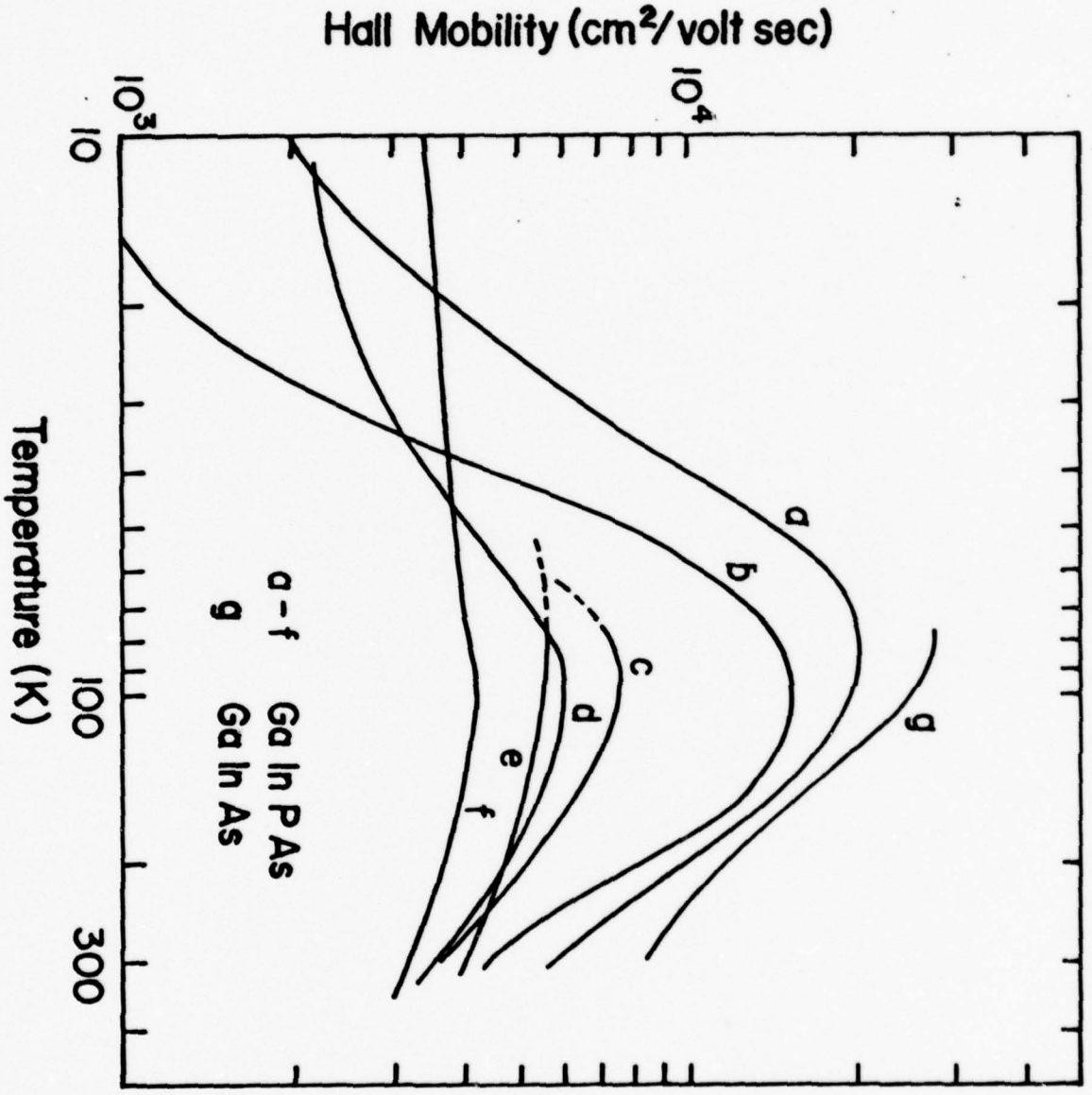
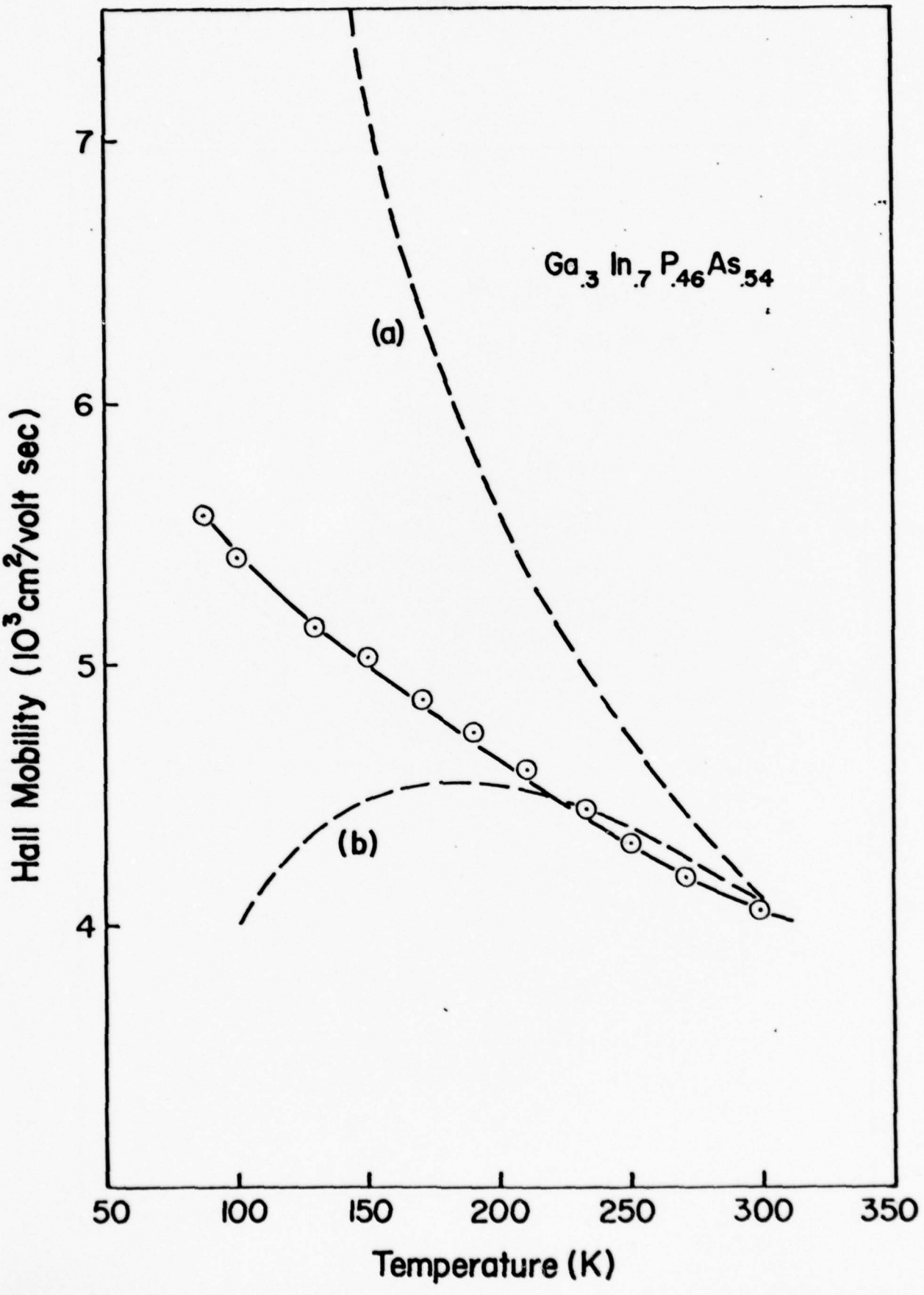
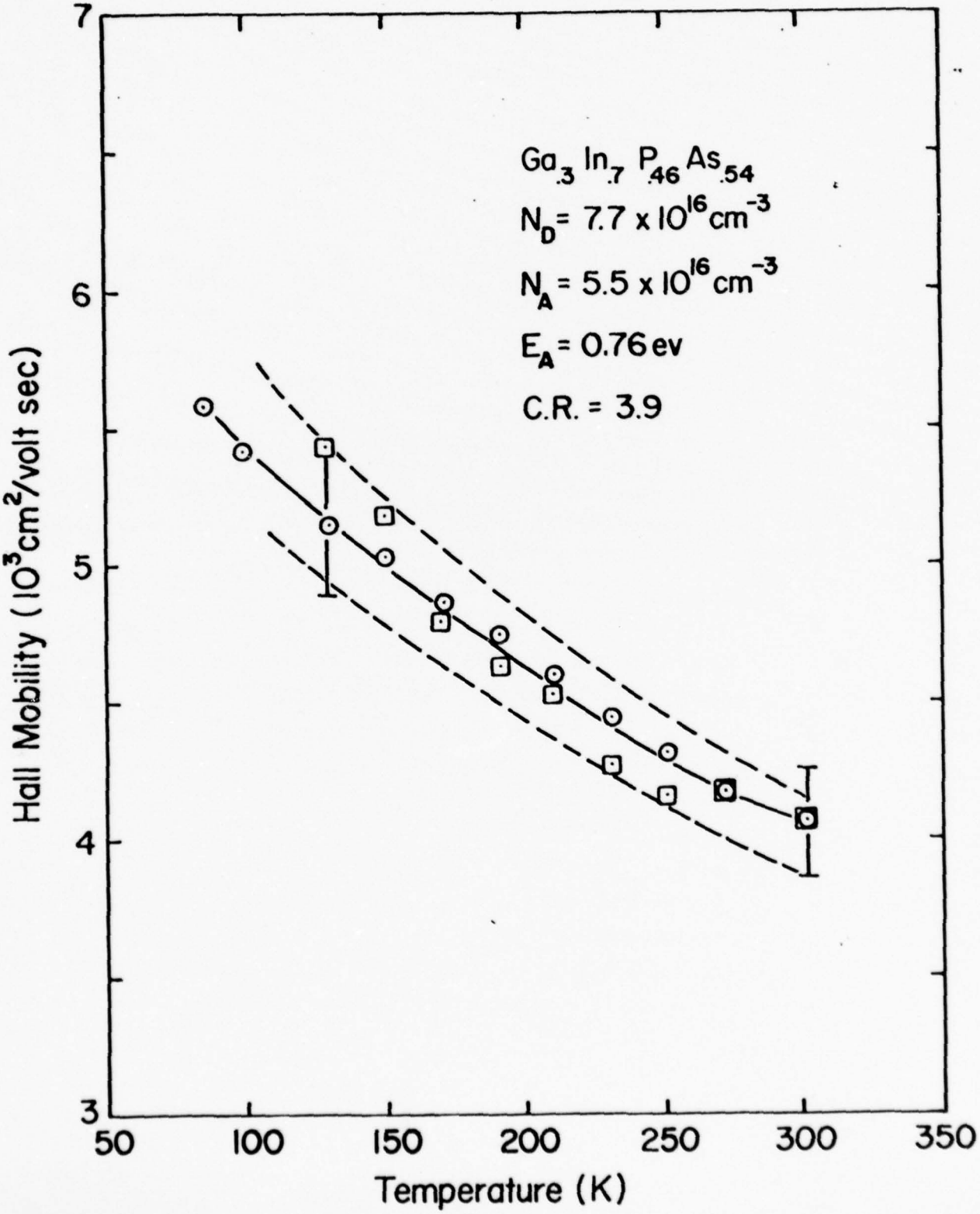

Ga_{1-x} In_x P_{1-y} As_y lattice-matched to InP
⊙ Restorff et al 1978
(a)
(b)
(c)
Effective Mass Ratio
.08
.07
.06
.05
.04
.03
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
As Composition

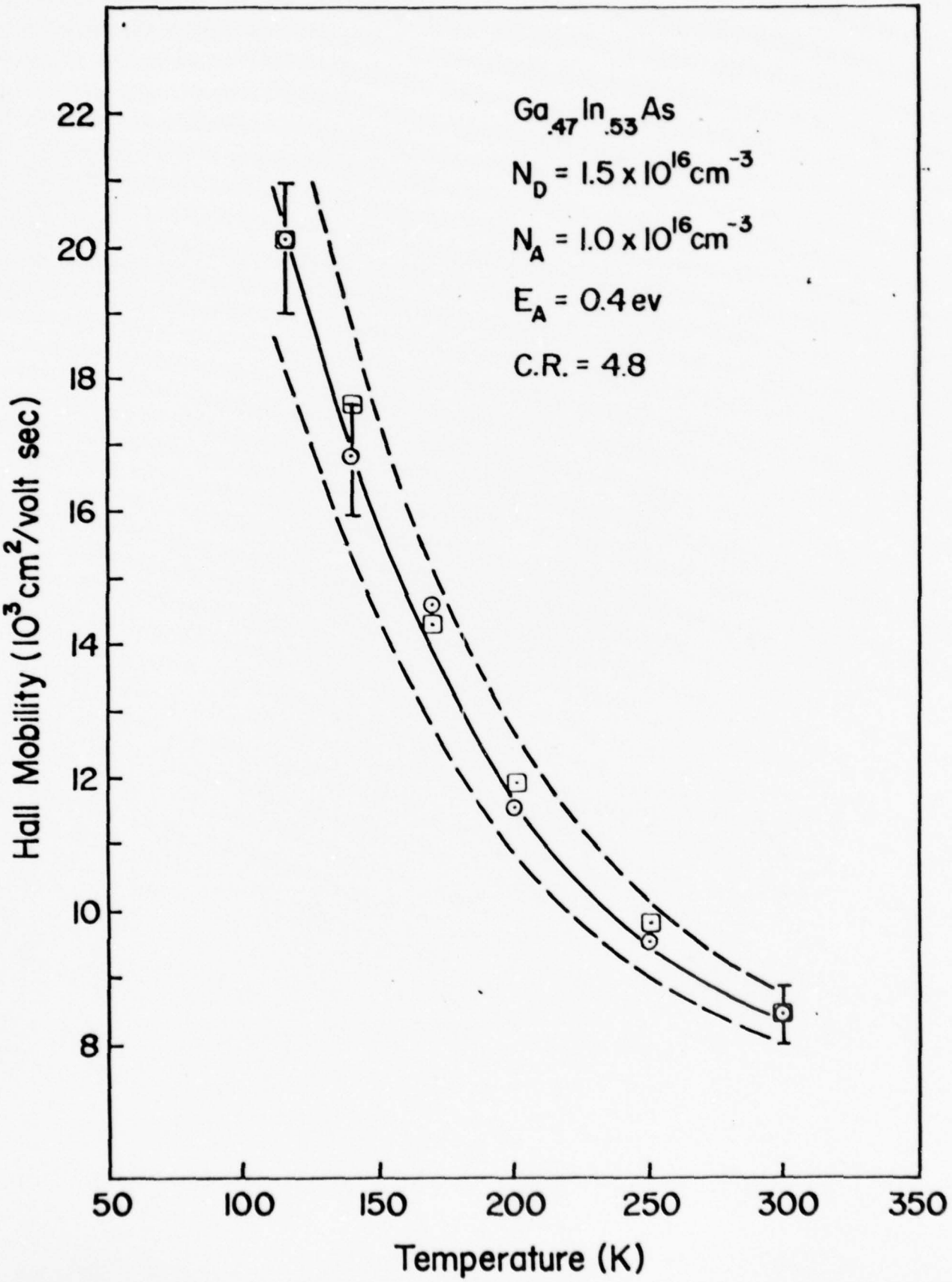

Hall Mobility (10^3cm^2/volt sec)
1
2
3
4
5
6
7
8
9
10
10^{14}
10^{15}
10^{16}
10^{17}
10^{18}
10^{19}
Carrier Concentration (cm^{-3})
Monte Carlo
Iterative Integral
Data from Sze 1969
(GaAs)
$Ga_{.27}In_{.73}P_{.4}As_{.6}$


GaAs
Monte Carlo
Iterative Integral
Hall Mobility (cm²/volt sec)
10³
10⁴
10⁵
10
100
1000
Temperature (K)


Hall Mobility (cm²/volt sec)
10³
10⁴
10
100
300
Temperature (K)
a-f Ga In P As
g Ga In As
a
b
c
d
e
f
g


Ga .3 In .7 P .46 As .54
(a)
(b)
Hall Mobility (10^3cm^2/volt sec)
7
6
5
4
50
100
150
200
250
300
350
Temperature (K)


$Ga_{.3}\,In_{.7}\,P_{.46}\,As_{.54}$
$N_D = 7.7 \times 10^{16} cm^{-3}$
$N_A = 5.5 \times 10^{16} cm^{-3}$
$E_A = 0.76 ev$
C.R. = 3.9
Hall Mobility ($10^3 cm^2$/volt sec)
Temperature (K)
7
6
5
4
3
50
100
150
200
250
300
350


$Ga_{.47}In_{.53}As$
$N_D = 1.5 \times 10^{16} cm^{-3}$
$N_A = 1.0 \times 10^{16} cm^{-3}$
$E_A = 0.4$ ev
C.R. = 4.8
Hall Mobility ($10^3 cm^2$/volt sec)
22
20
18
16
14
12
10
8
50
100
150
200
250
300
350
Temperature (K)

3.2 Appendix B

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ENERGY BANDGAP AND LATTICE CONSTANT CONTOURS OF III-V QUATERNARY ALLOYS*

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Energy band gap and lattice constant contours are presented for the nine quaternary alloys formed from Al, Ga, In and P, As, Sb. The quaternary bandgaps were obtained using an interpolation formula proposed by Moon et al. The quaternary lattice constants were obtained by use of a linear interpolation technique using the binary lattice constants as boundary values.

Key words: quaternary alloys, bandgap, lattice constant.

Introduction

There has been considerable interest in the quaternary III-V semiconductor materials for many applications, such as electro-optics and microwave devices [1-6]. One significant reason for this interest is the ability to synthesize materials with a fixed lattice constant and a variable range of energy bandgaps or, conversely, to synthesize materials with a constant energy bandgap and a variable lattice constant [7].

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In order to predict the energy bandgap or lattice constant for a quaternary material a two-step sequence is involved. Initially, it is necessary to have available experimental (or theoretical) values of these material parameters for the four possible binary III-V constituents of the quaternary compound. These values are readily available for most III-V materials in the literature [8]. There are also four possible ternary (pseudobinary) III-V systems in a given quaternary compound. In the first step, the energy bandgap and lattice constant as a function of alloy composition for each ternary system is computed from the known binary material parameters. This computation is on a good experimental and theoretical basis [9-13] involving the use of Vegard's law and the concept of the "bowing parameter" for the energy bandgap [14]. The final step involves the use of the compositional dependence of the energy bandgap and lattice constant for the four ternary combinations to interpolate to the desired quaternary energy bandgap and lattice constant. This final interpolation step is somewhat empirical in nature. There appear to be several such interpolation techniques used in the literature [6,7,15] and while these are similar, they also have non-trivial differences. This paper will discuss this critical interpolation procedure in view of the small amount of experimental quaternary data, and will present calculations for energy bandgaps and lattice constants for the nine quaternary alloys formed from Al, Ga, In and P, As, Sb using one of these interpolation techniques.

Notation

There appears to be no generally-accepted scheme for symbolically describing the III-V quaternary alloys. In this paper the following convention has been adopted. Within both the group III and group V pairing, the first position is occupied by the element with lowest atomic number. The composition variables are associated with the four elements in the order 1-x, x, 1-y, y. For example, a quaternary alloy will be denoted as $A_{1-x}B_xC_{1-y}D_y$. Here A and B are group III elements with A having lower atomic number than B. Likewise, C and D are group V elements with C having lower atomic number than D. Following previous authors [6,7], a quaternary alloy parameter (e.g., bandgap or lattice constant) is described by a surface Q(x,y) over

the x,y composition plane ($0 \leq x \leq 1$, $0 \leq y \leq 1$). At the corners (x and y equal to zero and/or one) the values of the parameter for the four binary elements $Q(0,0) = B_1$, $Q(1,0) = B_2$, $Q(1,1) = B_3$ and $Q(0,1) = B_4$ are obtained. Along the boundaries of the plane the parameter for the four ternary elements $Q(x,0) = T_{12}(x)$, $Q(1,y) = T_{23}(y)$, $Q(x,1) = T_{43}(x)$ and $Q(0,y) = T_{14}(y)$ are obtained.

Estimation of Alloy Parameters

Many ternary alloy parameters (e.g. lattice constant) are obtained by linear interpolation from those of the constituent binary compounds, i.e.,

$$T_{ij}(x) = xB_j + (1-x)B_i \tag{1}$$

For some parameters the theoretical variation with composition is nonlinear [14,16]. For the direct bandgap for example, Thompson and Woolley [9] have shown that

$$T_{ij}(x) = xB_j + (1-x)B_i - C_{ij}x(1-x) \tag{2}$$

where C_{ij} is the bowing parameter for the ternary alloy bandgap T_{ij}.

In the absence of definitive theories for quaternary parameters, estimates of a quaternary alloy parameter $Q(x,y)$ must be obtained by interpolation from the four ternary alloy parameters T_{ij}. Various interpolation schemes have been proposed. Onton and Chicotka [15] used the solution of Laplace's equation subject to the boundary conditions $Q(x,0) = T_{12}(x)$, etc. In Monte Carlo transport studies [6] the present authors have used the interpolation equation

$$Q(x,y) = \frac{x(1-x)[(1-y)T_{12}(x)+yT_{43}(x)]+y(1-y)[(1-x)T_{14}(y)+xT_{23}(y)]}{x(1-x)+y(1-y)} \tag{3}$$

This interpolation equation reduces to the ternary parameters on the quaternary plane boundaries and to the average

of the ternary parameters at the midpoint (x=0.5,y=0.5) of the compositional plane. This is incidentally the solution to Laplace's equation if the T_{ij} are linear as in Eq. (1). Moon et al. [7] have proposed similar schemes for the estimation of lattice constant and bandgap. For the lattice constant, Moon gives (in the above notation)

$$Q(x,y) = B_1+(B_2-B_1)x + (B_4-B_1)y + (B_1-B_2+B_3-B_4)xy \quad (4)$$

For the lattice constant, the T_{ij} are assumed to be linear in their arguments, so the solution to Laplace's equation is identical to Eq. (3), which in turn also reduces to Eq. (4).

For the bandgap, Moon et al. have used the equation

$$Q(x,y) = (1-x)T_{14}(y) + x\,T_{23}(y) - \Delta \quad (5)$$

where the T_{ij} are determined from Eq. (1) and

$$\Delta = x(1-x)[(1-y)C_{12}+yC_{43}] + y(1-y)[(1-x)C_{14}+xC_{23}] \quad (6)$$

An important difference between this bandgap estimate and that obtained from Eq. (3) is in the manner in which the ternary bowing parameters C_{ij} enter the calculation. In Eq. (3), the ternary bowing effects are included in the T_{ij}, whereas in Moon's method the bowing enters as a separate quaternary bowing parameter term given in Eq. (6). At the center of the composition plane, Eq. (3) yields (for the quaternary bowing) 1/16 ($C_{12} + C_{43} + C_{14} + C_{23}$) and Eq. (5) gives 1/8 ($C_{12} + C_{43} + C_{14} + C_{23}$), which is twice as large. Thus, at the center, Eq. (3) gives the average of the bowing contributions from the four ternaries, whereas Eq. (5) gives the average of the bowing contributions from the two sublattices. This is the principle difference between the interpolation schemes of Refs. 6 and 7.

Comparison with Experiment

Onton and Chicotka compared their interpolation approach (solution to Laplace's equation) with measured values of the quaternary bandgap in $Ga_{1-x}In_xP_{1-y}As_y$ and found the interpolated values to be within ±30 meV of the measured values. We have repeated this comparison, using their measured data. The results are given in Table 1. The average error and standard deviation of the error are also shown, and it is seen that Eqs. (3) and (5) give comparable errors.

Table I. Comparison of Eqs (3) and (5) with Experimental Data for $Ga_{1-x}In_xP_{1-y}As_y$.

Composition		Bandgap (eV)		
x	y	Eq (3)	Eq (5)	Measured [15]
0.004	0.260	2.357	2.353	2.222
0.006	0.340	2.244	2.239	2.124
0.006	0.420	2.136	2.131	1.993
0.009	0.500	2.027	2.020	1.881
0.008	0.590	1.913	1.907	1.738
0.010	0.710	1.763	1.755	1.592
0.012	0.830	1.619	1.609	1.475
0.017	0.910	1.521	1.510	1.351
0.015	0.970	1.455	1.447	1.326
0.060	0.220	2.336	2.297	2.203
0.060	0.280	2.255	2.214	2.135
0.070	0.340	2.160	2.113	2.038
0.080	0.440	2.014	1.963	1.869
0.110	0.650	1.709	1.650	1.535
0.110	0.700	1.649	1.591	1.472
0.170	0.850	1.383	1.326	1.236
0.190	0.975	1.184	1.166	1.165
0.250	0.140	2.124	2.054	2.101
0.230	0.190	2.100	2.021	2.041
0.250	0.240	2.008	1.921	1.953
0.250	0.310	1.924	1.830	1.809
0.260	0.630	1.523	1.430	1.388
0.330	0.800	1.225	1.145	1.170
0.340	0.090	2.029	1.971	2.077

Table I continued.

Composition		Bandgap (eV)		
x	y	Eq (3)	Eq (5)	Measured [15]
0.370	0.120	1.954	1.883	1.978
0.410	0.170	1.843	1.757	1.850
0.400	0.030	1.983	1.957	2.086
0.460	0.040	1.887	1.854	2.019
0.500	0.040	1.830	1.797	1.953
0.570	0.060	1.723	1.678	1.854
0.650	0.060	1.625	1.580	1.750
0.710	0.060	1.558	1.513	1.686
0.830	0.100	1.401	1.346	1.470
0.870	0.130	1.333	1.276	1.389
0.920	0.190	1.216	1.166	1.268
Average error (eV)		-0.052	-0.008	
rms error (eV)		0.109	0.118	

Calculation of Lattice Constant and Bandgap

For the calculation of the lattice constant, the three methods discussed above are identical, as given in Eq. (4). For the calculation of the bandgap, we have elected to use Moon's procedure, since it has some theoretical basis, whereas the other two are more or less ad hoc.

The quaternary lattice constant and energy bandgap contours are presented in Figure 1(a)-(i). These contours were obtained by numerical solutions of Eqs. (4) and (5), using the data given in Table 2. In all cases, the lowest quaternary bandgap is plotted in Figure 1. The shaded regions represent compositions for which the quaternary alloy is an indirect bandgap material.

Estimation of Unknown Ternary Bowing Constants

Relatively few of the III-V ternary bowing constants are known with any certainty, especially for the X(100) and L(111) valleys. Figure 2 shows the reported bowing parameters for several ternary materials as a function of the lattice constant difference between the two end-point binary compounds. While there is some uncertainty in the experimental data there does appear to be a definite trend toward larger bowing parameters with larger lattice constant differences. The solid line relationship shown in Figure 2 has been used to estimate several unknown bowing constants, as identified by the asterisks in Table 2. Since bowing is known to occur, it was felt that this procedure is better than arbitrarily setting the unknown bowing constants to zero.

Summary

Calculated bandgap and lattice constant contours have been presented for nine quaternary III-V material systems. The calculated values are based upon interpolation techniques which use known values of ternary III-V parameters to estimate the bandgap and lattice constant parameters for the quaternary systems. Since there is some uncertainty in both the ternary parameters and the best interpolation technique these calculated values must be considered as first order approximations until more experimental data is obtained for the quaternary systems. However, the curves should prove useful for many studies of the general properties of the increasingly important III-V quaternary materials.

Acknowledgments

We would like to express our appreciation to J. Shade for his assistance in this work.

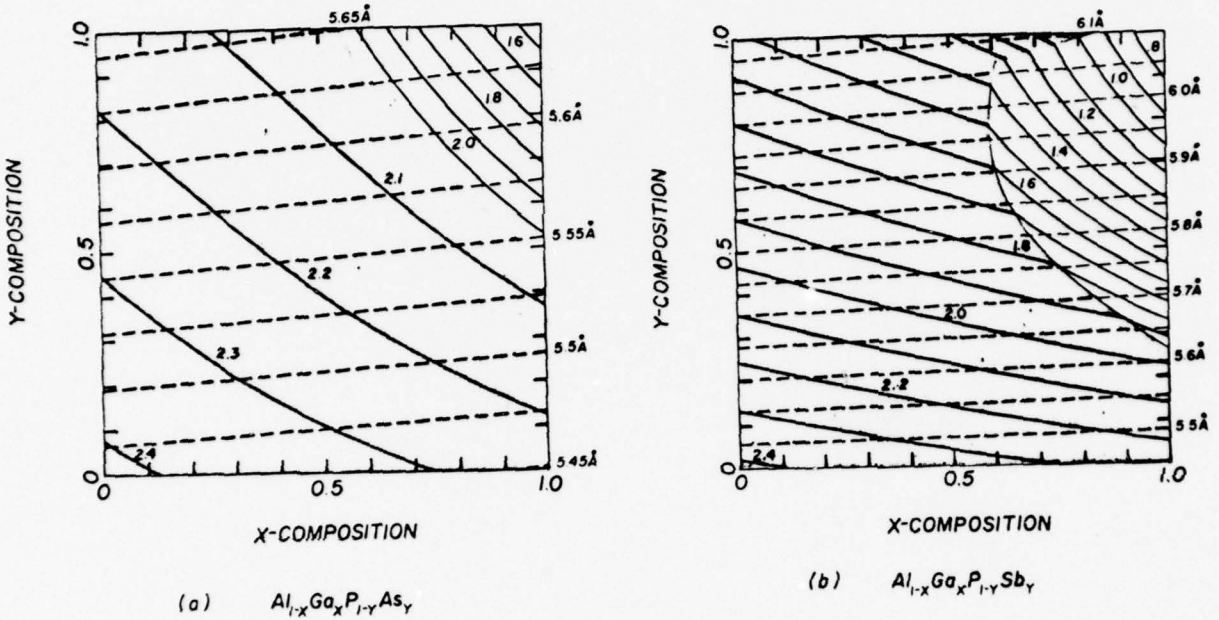
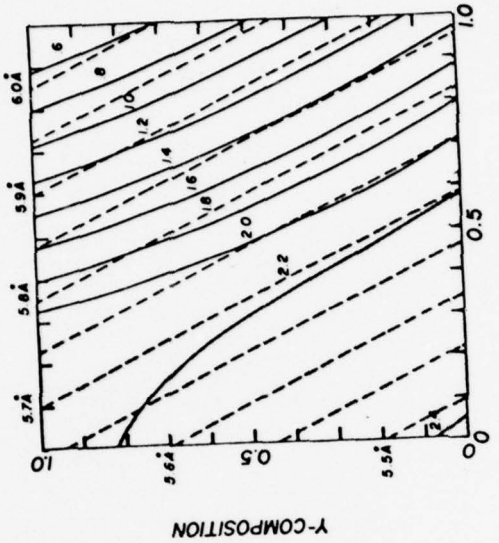
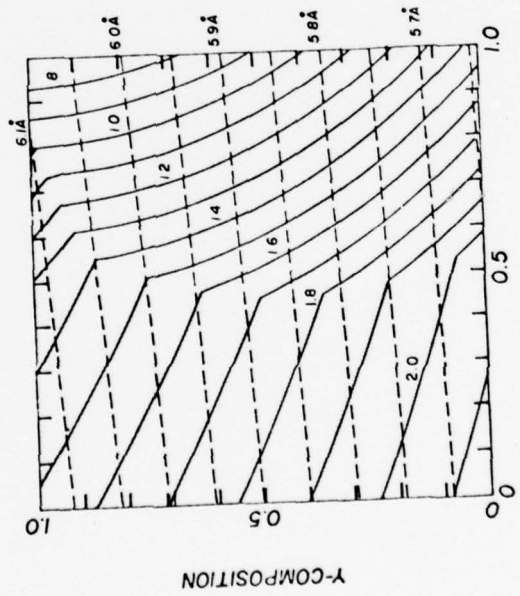


Figure 1. Energy bandgap and lattice constant contours for III-V quaternary alloys. The solid curves are the energy gap contours and the dashed curves are lattice constant contours. The shaded region shows the compositional range over which the material has an indirect bandgap.

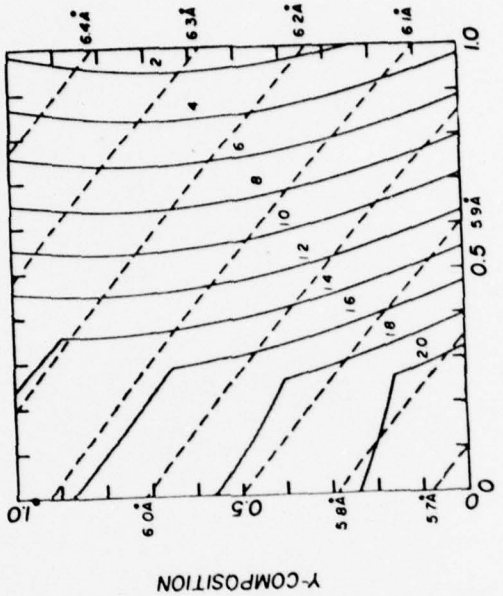


(d) $Al_{1-x}In_xP_{1-y}As_y$

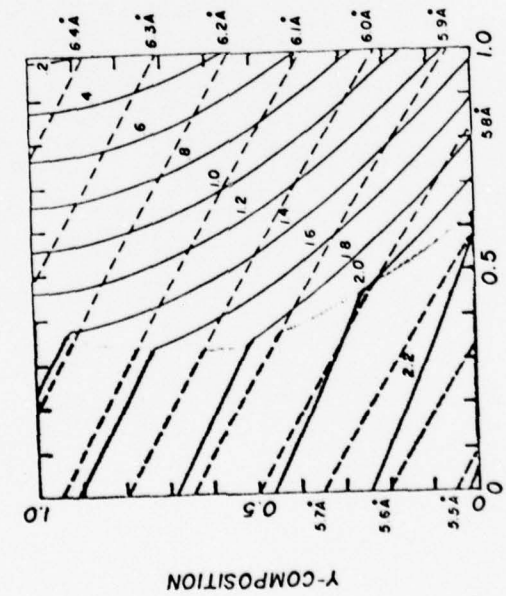


(c) $Al_{1-x}Ga_xAs_{1-y}Sb_y$

Figure 1 (continued)

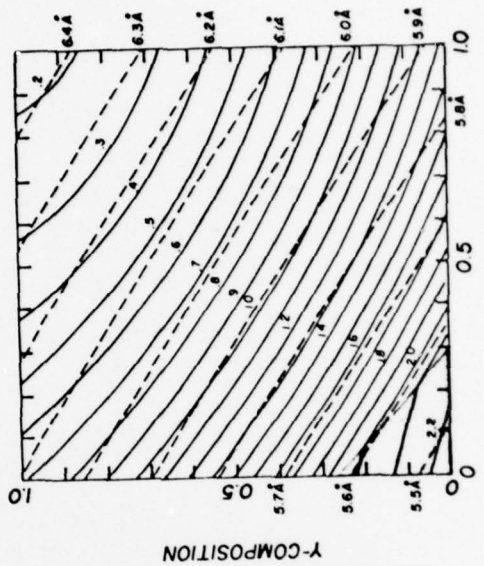


(f) $Al_{1-x}In_xAs_{1-y}Sb_y$

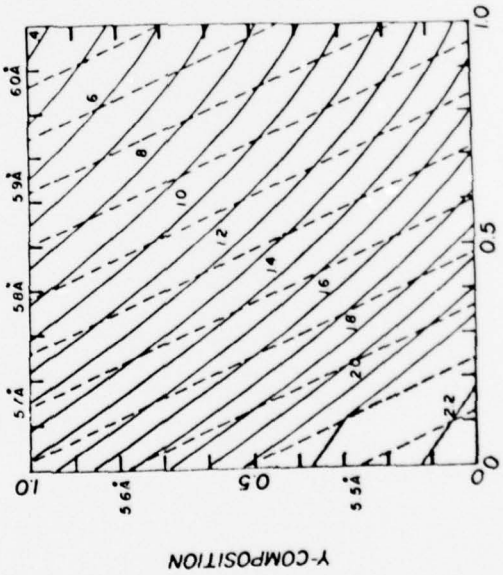


(g) $Al_{1-x}In_xP_{1-y}Sb_y$

Figure 1 (continued)

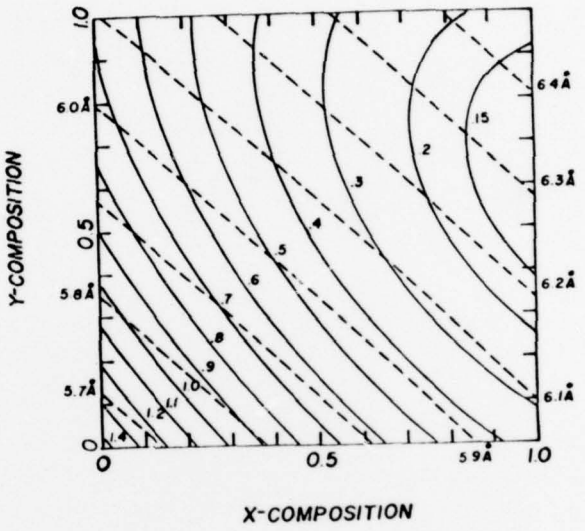


(h) $Ga_{1-x}In_xP_{1-y}Sb_y$



(g) $Ga_{1-x}In_xP_{1-y}As_y$

Figure 1 (continued)



(i) $Ga_{1-X}In_XAs_{1-Y}Sb_Y$

Figure 1 (continued)

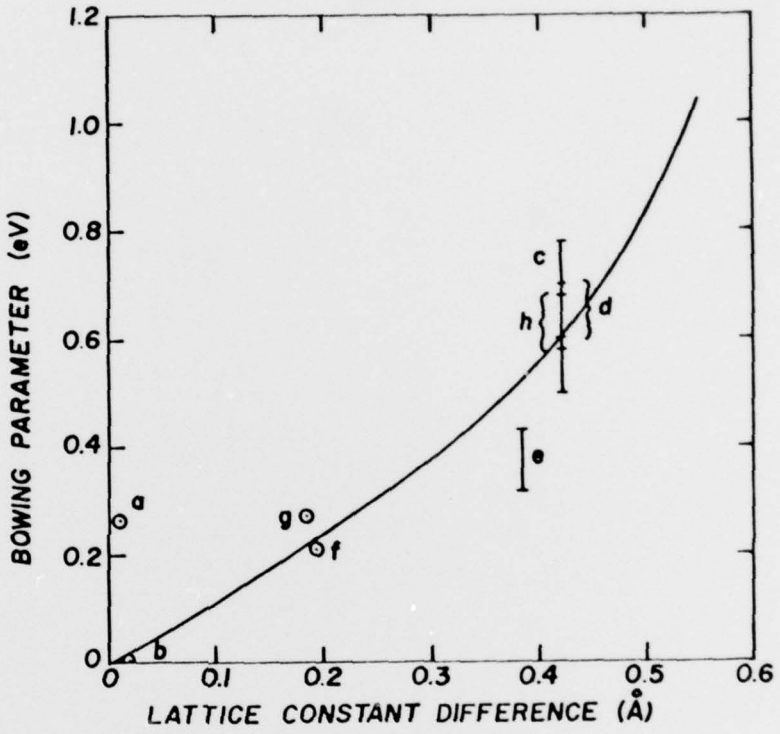


Figure 2. Experimental bowing parameters versus lattice constant difference for III-V ternary alloys. (a) $Al_{1-x}Ga_xAs$, (b) $Al_{1-x}Ga_xSb$, (c) $Ga_{1-x}In_xP$, (d) $Ga_{1-x}In_xAs$, (e) $Ga_{1-x}In_xSb$, (f) $GaP_{1-x}As_x$, (g) $InP_{1-x}As_x$, (h) $InAs_{1-x}Sb_x$.

References

1. J. S. Etcher, G. A. Antypas, and J. Edgecombe, Appl. Phys. Lett. 29, 153 (1976).

2. P. D. Wright, J. J. Coleman, N. Holonyak, M. J. Ludowisc, and G. E. Stillman, Appl. Phys. Lett. 29, 18 (1976).

3. J. J. Hsieh, J. A. Rossi, and J. P. Donnelly, Appl. Phys. Lett. 28, 709 (1976).

4. T. P. Pearson, B. I. Miller, R. J. Clark, K. J. Bachmann, Appl. Phys. Lett. 28, 499 (1976).

5. C. J. Neuse, Technical Digest IEDM, Washington, D.C., p. 125, Dec. 1976.

6. M. A. Littlejohn, J. R. Hauser, and T. H. Glisson, Appl. Phys. Lett. 30, 242 (1977).

7. R. L. Moon, G. A. Antypas, and L. W. James, J. Electron. Mater. 3, 635 (1974).

8. M. Neuberger, Handbook of Electronic Materials, vol. 2, III-V Semiconducting Compounds (IFI/Plenum, New York, 1971).

9. A. G. Thompson and J. C. Woolley, Can. Jour. Phys. 45, 255 (1967).

10. J. A. Van Vechten and T. K. Bergstresser, Phys. Rev. B 1, 3351 (1970).

11. K. S. Song, Solid State Commun. 13, 1397 (1973).

12. M. Altarelli, Solid State Commun. 15, 1607 (1974).

13. A. Onton, Jour. Luminescence 7, 95 (1973).

14. J. W. Harrison and J. R. Hauser, Phys. Rev. B 13, 5347 (1976).

15. A. Onton and R. J. Chicotka, International conf. on Luminescence, Leningrad, 1972.

References continued.

16. J. W. Harrison and J. R. Hauser, Jour. Appl. Phys. 47, 292 (1976).

3.3 Appendix C

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ENERGY BANDGAP AND LATTICE CONSTANT CONTOURS OF III-V QUATERNARY ALLOYS OF THE FORM $A_xB_yC_zD$ or $AB_xC_yD_z$*

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Energy bandgap and lattice constant contours are presented for the six quaternary alloys formed from Al, Ga, In and P, As, Sb, with compositions of the form $A_xB_yC_{1-x-y}D$ or $AB_xC_yD_{1-x-y}$. The quaternary bandgaps and lattice constants were obtained using an interpolation formula proposed by the present authors.

Key words: quaternary alloys, bandgap, lattice constant.

Introduction

In a previous paper [1], bandgap and lattice constant contours for nine III-V quaternary alloys have been presented. The present paper extends that work to include six additional quaternary alloys. Most of the work done on III-V quaternary materials has been on one or more of the nine quaternary alloy systems consisting of two elements from group III and two elements from group V. These are hereafter referred to as 2:2 quaternary alloys. There has

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been some interest [2,3,4] in the set of III-V quaternary alloy systems that are formed by selecting either three group III elements and one group V element, or one group III element and three group V elements. These are hereafter referred to as 3:1 or 1:3 quaternary alloys. This paper presents energy bandgap and lattice constant contours for the six 3:1 and 1:3 quaternary alloys formed from Al, Ga, In and P, As, Sb. The calculations are based on an interpolation procedure which is similar to the one previously applied to the nine 2:2 quaternary alloys [1].

Notation

There has been very little published material on the 3:1 and 1:3 III-V quaternary alloy systems, and there is no generally-accepted scheme for symbolically describing the composition of such materials. In this work the following convention is adopted: the composition variables associated with the three variable elements are in the order x, y, and z. These are constrained by

$$x + y + z = 1. \tag{1}$$

A 1:3 quaternary alloy will be described as $AB_xC_yD_z$, where A is a group III element and B, C and D are group V elements listed according to increasing atomic number. A 3:1 quaternary alloy will be described as $A_xB_yC_zD$, where A, B and C are group III elements listed in increasing atomic number and D is a group V element. A 3:1 or 1:3 quaternary alloy parameter is described by a surface Q(x,y,z) over the triangular composition plane ($0<x<1$, $0<y<1$, $0<z<1$; $x+y+z=1$) shown in Figure 1. At the corners, the values of the parameter for the three binary compounds $Q(1,0,0)=B_1$, $Q(0,1,0) = B_2$ and $Q(0,0,1) = B_3$ are obtained. Along the boundaries of the plane the parameters for the three ternary alloys $Q(x,y,0) = T_{12}(u)$, $Q(0,y,z) = T_{23}(v)$, and $Q(x,0,z) = T_{13}(w)$ are obtained, where

$$u = (1-x+y)/2,$$

$$v = (1-y+z)/2, \tag{2}$$

$$w = (1-x+z)/2.$$

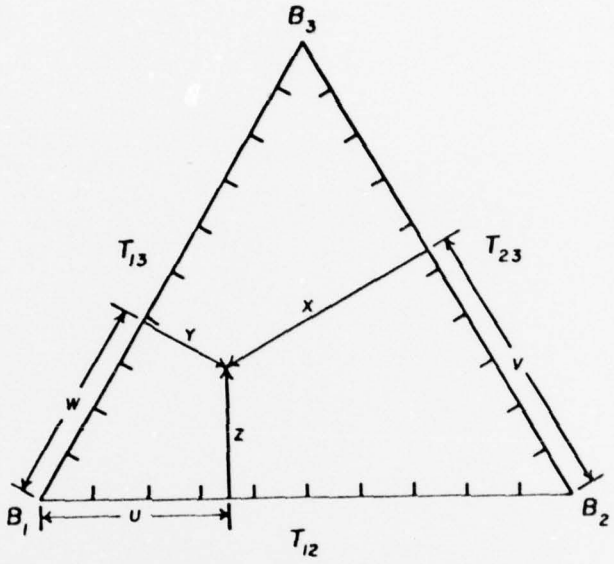

Fig. 1. Illustrating the definitions of the ternary (u,v,w) and quaternary (x,y,z) alloy composition variables.

Estimation of Alloy Parameters

As in the previous paper on 2:2 quaternary alloys [1], the lattice constants of the ternary alloys are linearly interpolated from the constituent binary components as,

$$T_{ij}(x) = xB_j + (1-x)B_i, \tag{3}$$

and the bandgaps of the ternary alloys are obtained using a nonlinear interpolation

$$T_{ij}(x) = xB_j + (1-x)B_i + C_{ij}x(1-x), \tag{4}$$

where C_{ij} is the bowing parameter for the ternary alloy bandgap T_{ij}. The quaternary alloy parameter $Q(x,y,z)$ is interpolated from the ternary parameters as

$$Q(x,y,z) = \frac{yxT_{12}(u) + yzT_{23}(v) + xzT_{13}(w)}{xy+yz+xz} \qquad (5)$$

Here the T_{ij} are the ternary alloy bandgaps or lattice constants given by Eq. (3) or (4), respectively, and the variables u, v, and w are as defined in Eq. (2). The quaternary parameters calculated according to Eq. (5) reduce to the appropriate ternary parameters on the triangle boundaries (x or y or z equal to zero) and to the average of the three ternary parameters at the center (x=y=z=1/3) of the composition plane.

Calculation of Contours

The 3:1 and 1:3 quaternary lattice constant and energy bandgap contours are presented in Figures 2(a)-(f). The contours were obtained by numerical solution of Eqs. (3), (4) and (5), using the data given in Table 1 of [1]. In all cases, the lowest quaternary bandgap is plotted in Figure 2. The shaded regions represent compositions for which the quaternary alloy is an indirect bandgap material.

Summary

Energy bandgap and lattice constant contours for the six III-V 3:1 and 1:3 quaternary alloy systems have been presented. Since little experimental work has been done with these materials, verification of the calculations cannot be made at the present time. However, the calculated parameters should be reasonably good first approximations which should prove useful in further investigations, realizing that Vegard's law seems to apply for these materials [4], that the interpolation procedure seems to be accurate for the 2:2 quaternaries [1], and that the values along the triangular composition boundary are based on ternary experimental data.

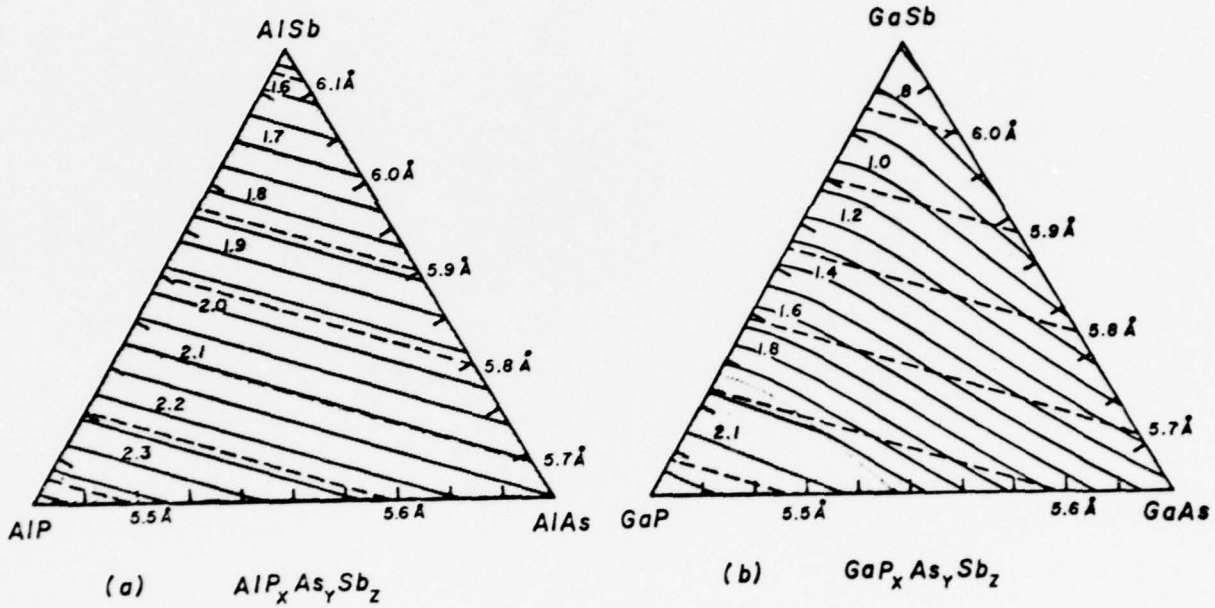

Fig. 2. Energy bandgap (solid lines) and lattice constant (dashed lines) contours for the 1:3 and 3:1 quaternary alloys. The energy bandgaps are in eV. The shaded regions are the compositions for which the quaternary alloy is an indirect material.

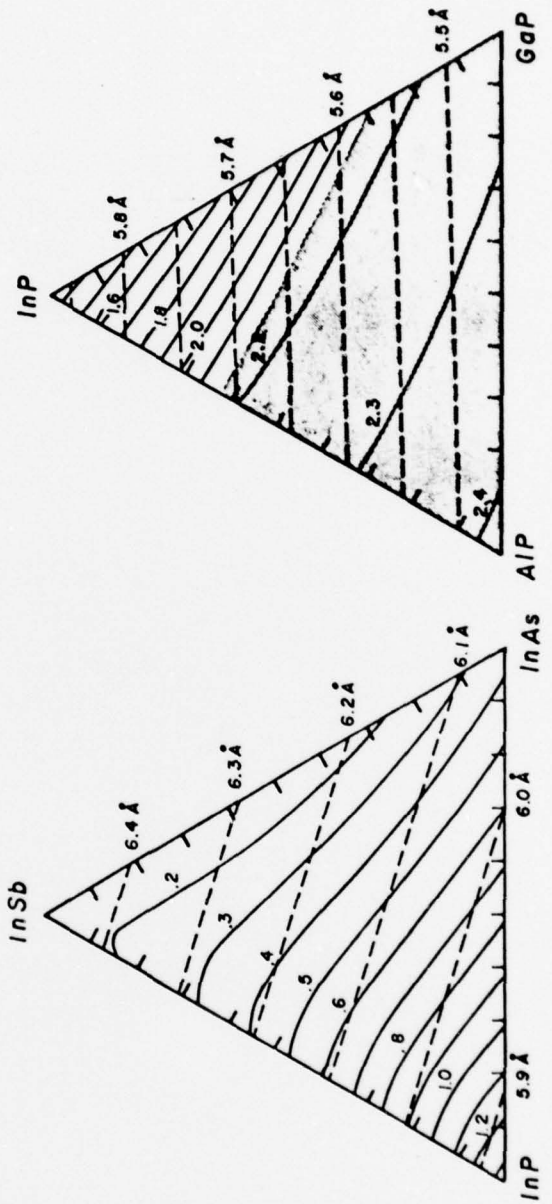

Fig. 2 (continued)

Fig. 2 (continued)

References

1. T. H. Glisson, J. R. Hauser, M. A. Littlejohn, and C. K. Williams, J. Electron. Mater. 7, 1(1978).

2. K. Nakajima, K. Osamura, and Y. Murakami, J. Electrochem. Soc. 122, 9 (1975).

3. H. Nagai and Y. Noguchi, J. Appl. Phys. 47, 12 (1976).

4. R. E. Nahory, M. A. Pollock, and J. C. DeWinter, J. Appl. Phys. 48, 1 (1977).

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